

UNLIMITED DISTRIBUTION



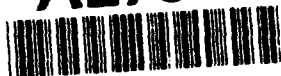
**National Defence**  
Research and  
Development Branch

**Défense nationale**  
Bureau de recherche  
et développement

TECHNICAL MEMORANDUM 93/214

October 1993

**AD-A273 164**



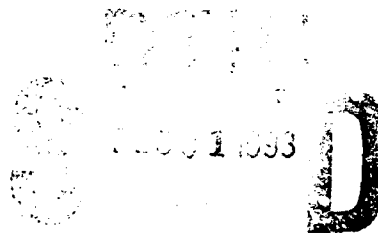
THE EFFECTS OF ZINC BORATE ADDITION ON  
THE FLAMMABILITY CHARACTERISTICS OF  
POLYESTER, VINYL ESTER AND EPOXY GLASS  
REINFORCED PLASTICS

Richard M. Morchat

**93-29356**



2488



**Defence  
Research  
Establishment  
Atlantic**



**Centre de  
Recherches pour la  
Défense  
Atlantique**

**Canada**

93 1 30 062

UNLIMITED DISTRIBUTION



**National Defence**  
Research and  
Development Branch

**Défense nationale**  
Bureau de recherche  
et développement

**THE EFFECTS OF ZINC BORATE ADDITION ON  
THE FLAMMABILITY CHARACTERISTICS OF  
POLYESTER, VINYL ESTER AND EPOXY GLASS  
REINFORCED PLASTICS**

Richard M. Morchat

October 1993

Approved by R.T. Schmitke  
Director / Technology Division

Distribution Approved by

Director / Technology Division

**TECHNICAL MEMORANDUM 93/214**

**Defence  
Research  
Establishment  
Atlantic**



**Centre de  
Recherches pour la  
Défense  
Atlantique**

**Canada**

## ABSTRACT

The effects of an inorganic fire-retardant additive, zinc borate, on flammability characteristics and smoke generation of glass reinforced polyester, vinyl ester and epoxy resins were evaluated. Information is presented on the flame spread index (ASTM E162), limiting oxygen index (ASTM D2863), density of smoke generated (ASTM E662) and toxic gases of combustion (Boeing BSS 7239).

Results indicated that the addition of 10 phr of zinc borate to the polymeric materials significantly decreased the flame spread index and increased the limiting oxygen index; however, the amount of smoke generated during pyrolytic and flaming combustion was high and unacceptable. Finally, the toxic gas evolution data indicated that the threshold limit values for some gases were exceeded.

## RÉSUMÉ

On a évalué les effets d'un additif ignifuge inorganique, le borate de zinc, sur les caractéristiques d'inflammabilité et le dégagement de fumée des résines époxydiques, de l'ester vinylique et du polyester renforcés de verre. On présente des données sur l'indice de propagation de la flamme (ASTM E162), l'indice limite d'oxygène (ASTM D2863), la densité de la fumée dégagée (ASTM E662) et les gaz de combustion toxiques (Boeing BSS 7239).

Les résultats indiquaient que l'addition aux matériaux polymériques de 10 parties de borate de zinc par cent parties de résine diminuait considérablement l'indice de propagation de la flamme et augmentait l'indice limite d'oxygène; toutefois, la quantité de fumée dégagée durant la combustion accompagnée de flamme et la combustion pyrolytique était élevée et inacceptable. Enfin, les données sur le dégagement de gaz toxiques indiquaient que, dans le cas de certains gaz, la TLV était dépassée.

## TABLE OF CONTENT

ABSTRACT.....	ii
TABLE OF CONTENT.....	iii
NOTATION.....	iv
1. INTRODUCTION.....	1
2. EXPERIMENTAL PROCEDURE.....	3
2.1. Resins Evaluated.....	3
2.2. Laminate Fabrication.....	3
3. RESULTS AND DISCUSSION.....	3
3.1. Surface Flammability.....	4
3.2. Limiting Oxygen Index.....	5
3.3. Smoke Density.....	6
3.4. Toxic Gas Analysis.....	7
4. CONCLUSION.....	9
REFERENCES.....	10
Table 1.....	12
Table 2.....	12
Figures.....	13

Accession For	
NTIS CRA&I	<input checked="checked" type="checkbox"/>
DTIC TAB	<input type="checkbox"/>
Unannounced	<input type="checkbox"/>
Justification	
By	
Dist to follow	
Availability	
Dist	for
A-1	

DTIC QUALITY INSPECTED 1

## NOTATION

ASTM	American Society of Testing and Materials
°C	Degrees Celsius
FR	Fire Retardant
GRP	Glass Reinforced Plastic
mm	Millimeter
phr	Parts Per Hundred Resin
ppm	Parts Per Million
ZB	Zinc Borate

## 1. INTRODUCTION

Apart from the seas, the most terrifying enemy of the sailor is fire, the effects of which can be devastating. The April 1986 fire aboard the aircraft carrier HMS Illustrious, for example, virtually destroyed one of her main gearboxes and resulted in the ship being out of action for several months. Fire, on its own, very seldom will sink a ship, but the damage caused can be severe, especially with the incapacitating effect on the crew of the thick black smoke that is commonly associated with shipboard fires. During and after the Falklands conflict, the effects of fire became so frighteningly obvious to everyone that ship designers became intimately involved in modifications. Over the last six years, many modifications to reduce the effects of fire in RN ships have been implemented, such as fire curtains to help contain the spread of smoke, better materials for cabling and for mattresses to reduce the amount of smoke given off, and more effective fixed fire-fighting arrangements, to name but a few [1]. As a result of the experience of the USS Stark in the Persian Gulf in May 1987, the US Navy has implemented a number of fleetwide changes in fire control, including plans to increase the use of more fire-resistant materials in ship construction.

The feasibility of using a glass reinforced plastic (GRP) composite as a substitute for steel and aluminum in the construction of ships' superstructures is under active consideration by several NATO navies. When one compares GRP to the other two common structural building materials of naval vessels, obvious advantages for GRP can be identified. For example, GRP materials can be processed to have excellent thermal and mechanical properties, they have good resistance to corrosion and the marine environment, and most importantly, they have a high strength to weight relationship. However, their fire performance properties remain a serious concern.

As part of DREA's research program on fire safe materials for marine applications, we have studied several ways of improving the fire resistance of glass reinforced plastics, including the use of insulating materials on the exposed surface, the application of ceramics by plasma spray deposition technology and the addition of inorganic fire-retardant additives such as antimony trioxide. Due to its pronounced synergism with halogens, the use of antimony trioxide is a well-established method for increasing fire-retardancy with halogenated resins [2]. However, we have shown that although antimony trioxide is an excellent fire-retardant because of its ability to decrease flame spread and increase oxygen

index, it is quite ineffective at decreasing the amount of smoke that is generated during burning of polyester and vinyl ester resin systems [3].

We expanded our study to include a fire-retardant where the mechanism is based on release of "water of hydration" during decomposition, with the accompanying absorption of a considerable amount of heat. The fire-retardant chosen was alumina trihydrate, also known as hydrated alumina. This fire-retardant is unique in having a high proportion (35%) of chemically combined water and is a readily available refined mineral filler that shows the unique and desirable properties of imparting significant fire retardant and smoke suppressive qualities to reinforced polyester plastics. Our investigation [4] showed that the addition of the inorganic material, alumina trihydrate, affected the flammability characteristics and smoke generation of polyester, vinyl ester and epoxy GRP panels. In fact, the smoke density was the one parameter that was affected the most by the alumina trihydrate addition. There were measured decreases as high as 57% as well as increases of 35%; nevertheless, the maximum value for smoke density was high for all resins tested and thus unacceptable. A fire-retardant that also exhibited smoke suppression abilities needed to be evaluated.

Zinc borate is a unique multifunctional fire-retardant [5]. It can function as a flame-retardant and smoke suppressant. It is claimed to act as an efficient synergist of organic halogen sources, and in certain halogen containing resin systems such as unsaturated polyester and epoxy, the zinc borate can outperform antimony oxide. In halogenated polymers the zinc borate markedly increases the amount of char formed during combustion. The zinc species remain in the condensed phase and alter the pyrolysis chemistry by catalyzing the dehydro-halogenation and promoting cross-linking. This results in increased char formation and a decrease in both smoke production and flaming combustion. In addition, due to its unique glass forming ability zinc borate acts as an afterglow suppressant.

In the study reported herein, we investigated the effect that the addition of the inorganic fire retardant/smoke suppressant additive, zinc borate, to several polyester, vinyl ester and epoxy resins has on both the amount of smoke generated and on the time delay to reach the maximum allowable concentration of smoke. In addition, the effects of this additive on other fire properties were monitored, such as the flame spread index, the oxygen index, and toxic gas evolution.

## 2. EXPERIMENTAL PROCEDURE

### 2.1. Resins Evaluated

Five resins were evaluated in this study; Hetron 197AT, Hetron 27196, Hetron 692TP25 (Ashland Chemicals), Derakane 510A (Dow Chemical Canada Inc) and Epon 813 (Shell Canada). Information from the resin manufacturers' product data sheets indicated that: Hetron 197AT is a Class 1 fire-retardant, chemical resistant, heat resistant, unsaturated polyester; Hetron 27196 and Hetron 692TP25 are low viscosity, thixotropic, promoted, halogenated, flame retardant polyester resins; Derakane 510A is a corrosion resistant, chemical resistant, fire resistant vinyl ester; and Epon 813 is a low viscosity, chemically resistant bisphenol-A based epoxy resin. All the resins, with the exception of the Epon, were catalyzed with 0.15 phr (parts per hundred resin by weight) of the accelerator cobalt naphthenate (Nuodex DMR, Nuodex Canada Ltd) and 1.0 phr of methyl ethyl ketone peroxide catalyst (Lupersol DDM-9, Pennwalt). The Epon 813 was cured by the addition of 15 phr of the epoxy resin hardener Ancamine 1638 (Pacific Ancor Chemical).

Except for the epoxy resin (Epon 813), the other four resins (Hetron 197AT, Hetron 27196, Hetron 692TP25 and Derakane 510A) contained proprietary halogenated materials, and they derived their fire-retardancy characteristics through the chemical action of chlorine and/or bromine molecules in the solid and gas phases.

### 2.2. Laminate Fabrication

Panels, 1200 x 1200 x 6 mm nominal thickness (4 ft x 4 ft x 0.25 inch), were manufactured by the custom contact molding method (also known as hand lay-up method). The panels were constructed using 6 layers of 450 g/m<sup>2</sup> (1.5 oz/ft<sup>2</sup>) chopped strand mat "E-glass" cloth (FC M751-450, Fiberglas Canada Inc). The inorganic fire-retardant component, Firebrake® ZB from US Borax (2ZnO•3B<sub>2</sub>O<sub>3</sub>•5H<sub>2</sub>O) was added to the resin at 10 phr.

## 3. RESULTS AND DISCUSSION

The evaluation of the fire performance of the GRPs containing the selected fire-retardant was conducted using four standard fire test procedures. These included an evaluation of the ability for flames to spread over the material, an evaluation of the minimum oxygen concentration required to support combustion of the panels, an evaluation



of the amount of smoke and the associated visual obscuration created by a flaming and non-flaming panel, and an evaluation of toxic gas evolution.

### 3.1. Surface Flammability

The radiant panel surface flammability test (ASTM E162)[6] provides a procedure for measuring and comparing the surface flammability of materials when exposed to a prescribed level of radiant heat energy. The rate of travel of a flame front along the surface depends on the physical and thermal properties of the material, the method of mounting and orientation of the specimen, the type and magnitude of fire and heat exposure, the availability of air and the properties of the surrounding area [7]. The rate of flame spread is a very important property in the history of a fire in that it controls the time after ignition when a fire has grown to a "dangerous size." The ability to detect, fight or escape from a fire depends on the time before the fire reaches a "dangerous size," and thus the lower the flame spread, the greater the time for escape becomes [8].

Figure 1 shows the results of the radiant panel surface flammability test for the 10 panels tested (five resins, without and with fire-retardant). The flame spread index for the polyester and vinyl ester resins were relatively low (12-43), while the flame spread index value for the epoxy resin was high at 60. The addition of the fire-retardant lowered the flame spread index in varying degrees (8-42%) depending on the resin system evaluated. In most cases the addition of 10 phr zinc borate was sufficient to lower the flame spread index below the established guideline of 25 maximum. The one anomaly was the Epon 813 where the fire-retardant addition had a minimal effect on the flame spread index.

These observations can be rationalized by examination of the mechanisms at play. For example, the four polyester/vinyl ester resin systems contained proprietary halogenated fire-retardant organic resins. These halogen containing fire-retardant resins (RX) act by interfering with the burning process taking place in the gas phase. The combustion process comprises a series of free radical chain reactions that generate the high energy  $\text{OH}\cdot$  and  $\text{H}\cdot$  radicals by chain branching. These radicals are removed by the halogen containing fire-retardant [9].

The halogen radical,  $\text{X}\cdot$ , reacts to form the hydrogen halide  $\text{HX}$  that interferes in the gas phase with the free radical chain branching and propagation reactions associated with the key radicals responsible for the propagation of the combustion as follows:





In this way the highly reactive chain propagating species ( $H\bullet$  and  $OH\bullet$ ) are replaced by the relatively unreactive halogen radicals,  $X\bullet$ , which may themselves regenerate  $HX$  by hydrogen abstraction from the fuel as follows:



The observed decreases in flame spread index values, upon addition of zinc borate, for the resin systems with the proprietary halogenated fire-retardants, results from the additional interference to the radical chain mechanism caused by physical action. The mechanisms by which zinc borate is believed to operate are several fold. It is assumed that this additive performs as a flame retardant by forming a protective glass matrix at the burning surface of a flammable substrate. The hydrated zinc borate combines with halogen from the halogenated resin during pyrolysis to generate zinc oxychloride and zinc chloride, both known flame retardants [10]. In addition, this unique form of zinc borate releases 14% by weight water in the temperature range of 290-450°C.

### 3.2. Limiting Oxygen Index

The oxygen index determination (ASTM D2863)[11] measures the ignitability of materials by measuring the minimum concentration of oxygen in a mixture of oxygen and nitrogen flowing upwards in a test column that will just support flaming combustion measured under equilibrium conditions of candle-like burning. A small propane gas flame, which is inserted into the open end of the column, is used to ignite the test specimen. As the sample is burned, the energy feedback from the flame to the burning surface maintains the surface temperature required for pyrolysis of the polymer, and this supplies gaseous fuel to form a combustible mixture with the oxygen/nitrogen stream. As the oxygen concentration is decreased, the flame temperature decreases, resulting in a reduction to the heat feedback and the supply of fuel to the flame zone. The limiting oxygen index (LOI) is defined as

$$LOI = \frac{[O_2]}{[O_2] + [N_2]}$$

where [ ] is the volume concentration of each gas in the combined gas stream. At the critical oxygen concentration (the LOI), a sudden transition from active burning to extinction occurs.

In the standard test, the sample burns downward with a small laminar flame and the energy is quickly dissipated to the cool surroundings with little energy feed-back to support the combustion of the sample. This is in sharp contrast to the hot turbulent environment characteristic of most real fires. Thus, it has been suggested [12] that the oxygen index should be measured as a function of temperature and the temperature at which the limiting oxygen index equals 20.9 should be taken as a measure of material flammability. This variation to the ASTM procedure was not currently measured due to unavailability of a modified test instrument, but will be considered when such an instrument is available.

Figure 2 shows the results of oxygen index determination for the 10 panels tested. The data was grouped by resin type. The oxygen index for all five resins evaluated was above the value of 20.9. With no added fire retardant, the oxygen index values were in the range of 22-30. The addition of zinc borate raised the oxygen index values in varying degrees (11-43%) depending on the resin system evaluated. Similar results were reported when 4-8 phr of zinc borate was added to halogenated polyester resins. The LOI was observed to increase from 27 to 40 [13].

### 3.3. Smoke Density

The smoke evolution test (ASTM E662)[14] measures the degree of light or sight obscuration by photometrically measuring the specific optical density of smoke generated by a solid material under specific exposure conditions. The values obtained are important since they can be used to provide a measure of fire hazard. Escape from a burning enclosure is enhanced if the occupant can see the exits. Firefighters also have a better chance of fighting and extinguishing a fire if visibility is not limited.

The smoke density generated by the GRP samples was followed by the measurement of the specific optical density using the NBS Smoke Chamber. Among the parameters normally reported are:

- Ds<sub>1.5</sub>        -    Specific optical density after 1.5 minutes,
- Ds<sub>4.0</sub>        -    Specific optical density after 4.0 minutes,

$D_m$  - Maximum specific optical density anytime during the 20 minute test, and

$D_{m(corr)}$  -  $D_m$  corrected for incidental deposits on the optical surfaces.

The specific optical density values of  $D_{s1.5}$ ,  $D_{s4.0}$ ,  $D_m$  and  $D_{m(corr)}$  for the five resin systems during the flaming (F) and non-flaming (NF) modes were plotted as Figures 3-7. It can be seen that, all five resin systems yielded relatively similar results. The  $D_{s1.5}$  values were all below 200; however, the four minutes maximum optical density,  $D_{s4.0}$ , values were between 300 and 600 in the flaming mode and between 10 and 50 in the non-flaming mode. The maximum smoke density  $D_{m(corr)}$  values of the five systems, for both the flaming and non-flaming modes were quite high. In the majority of samples tested the addition of zinc borate resulted in a lowering of the specific optical density values in varying degrees (12-60%) depending on the resin system evaluated (Table 1). The one anomaly was Hetron 692TP25 in the flaming mode where the specific optical density actually increased by 32%. The lowest value measured approached 200; however, the guideline level of 200 maximum used by the transit industry was exceeded for most of the samples.

The lowest  $D_{m(corr)}$  value was observed for Epon 813 (Table 1) even though this resin had the highest value for flame spread index (Figure 1). This can be rationalized because as flaming combustion is favored, the amount of smoke generated usually decreases.

### 3.4. Toxic Gas Analysis

Toxic gases are an important cause of casualties in fires. A wide variety of toxic gases are produced in a fire, at levels that can be extremely hazardous, both as single gases and in combination of gases [15]. The composition of these gases varies considerably with types of resin used, additives used, and with varying fire conditions. When a polymer is heated, sufficient energy can be introduced into the polymer system to cause thermal degradation by breaking the bonds along the polymer chain. Gaseous molecules are released. The combustible gases, in the presence of an oxidizing agent (air), will ignite and produce a flame. Other gases may also be produced that are not combustible (eg.  $H_2O$ ,  $CO_2$  and  $SO_2$ ). Particles, primarily carbon, may also be emitted, leading to smoke production. These three components (unburned gases, burned gases and smoke) will be responsible for the direct toxic effects generated in a real fire situation.

The use of a flame-retardant additive may tend to increase the toxic emission problems by chemically changing the composition of the gases released in the fire situation. For example, a chlorine-containing additive will generate chlorine radicals which in an oxygen-rich condition can result in the formation of toxic phosgene. This would result in a completely different type of emission profile, with the evolution of new toxic compounds. In fact, many of the flame-retardant additives are themselves toxic at normal operating temperatures, and it is not expected that they will lose their toxicity at the higher temperatures experienced in a fire. Consequently, a study of the hazardous gases released by these resin systems when thermally degraded was conducted.

The last test conducted on the ten GRP panels involved the Boeing BSS 7239 toxic gas sampling [16]. In this test, the gases generated during the NBS Smoke Chamber evaluation are sampled at various intervals for the following components: Carbon Monoxide (CO), Hydrogen Bromide (HBr), Hydrogen Chloride (HCl), Hydrogen Cyanide (HCN), Hydrogen Fluoride (HF), Nitrogen Oxides (NO<sub>x</sub>) and Sulphur Dioxide (SO<sub>2</sub>). The results for Carbon Monoxide (CO), Hydrogen Bromide (HBr) and Hydrogen Chloride (HCl) are shown in Table 2. The values for CO<sub>max</sub>, the maximum concentration of CO in parts per million (ppm), as a function of resin without and with fire retardant are plotted in Figure 8. The transit industry guideline for carbon monoxide concentration is set at 3500 ppm. As can be seen from Figure 8, several of the resin systems have maximum CO levels near the 3500 ppm guideline, and this level is only slightly reduced through the addition of zinc borate. The two anomalies were the Hetron 27196 and Hetron 692TP25, where the CO<sub>max</sub> values actually increased upon addition of zinc borate.

High concentrations of two acid gases, HCl and HBr, were detected from the four resins that were known to contain proprietary halogenated fire-retardants. The values for HCl<sub>max</sub>, the maximum concentration of HCl in ppm, as a function of resin without and with fire retardant are plotted in Figure 9. It can be seen (Table 2) that Hetron 197AT and Hetron 27196 are heavily loaded with a chlorinated additive, while Derakane 510A contains a brominated species. Epon 813, which was known not to contain any fire-retardant, did in fact generate small quantities of these two gases.

The other gases monitored were produced in very low concentrations and would not be significant contributors to the overall toxicity of the fire gases.

It was apparent from the results that smoke density was the one parameter that was affected the least by the zinc borate addition. This parameter still remains too high to be

acceptable and further studies will be aimed at lowering the smoke. "New and improved" polyester resins, other fire-retardants and smoke-suppressants, and other thermoset resins such as phenolics will be investigated as a means by which smoke generation can be lowered.

#### 4. CONCLUSION

This investigation showed that the addition of the inorganic material, zinc borate, affected the flammability characteristics and smoke generation of polyester, vinyl ester and epoxy GRP panels. For example, the addition of 10 phr zinc borate to resins containing halogenated fire-retardant additives lowered the flame spread index to values below the transit industry's upper acceptable guideline. The limiting oxygen index increased with all resin systems upon addition of zinc borate. The smoke density was the one parameter that was affected the most by the zinc borate addition. There were measured decreases as high as 60% as well as increases of 32%; nevertheless, the  $Dm_{(corr)}$  values were high for most resins tested and thus unacceptable. Finally, the toxic gas evolution data indicated that the threshold limit values for some gases, in particular the acid gases, were exceeded.

## REFERENCES

- 1 Maclean, M., "Naval Accidental Losses-A 25 Year History", Navy International, 24, 93, 1989.
- 2 Antia, F.K., Baldry, P.J. and Hirschler, M.M., "Comprehensive Study of the Effect of Composition on the Flame Retardant Activity of Antimony Trioxide and Halogenated Hydrocarbons in Thermoplastic Polymers", Eur Polym J., 18, 167, 1982.
- 3 Morchat, R.M., "The Effect of Antimony Trioxide Addition on the Flammability Characteristics of Polyester and Vinyl Ester Glass Reinforced Plastics," DREA Technical Memorandum 89/213, May 1989.
- 4 Bonsignore, P.V. and Manhart, J.H., "Alumina Trihydrate as a Flame Retardant and Smoke Suppressive Filler in Reinforced Polyester Plastics," 29th Annual Technical Conference, Reinforced Plastics/Composites Institute, Paper 23-C, 1974.
- 5 Shen, K.K. and Griffin, T.S., "Zinc Borate as a Flame Retardant, Smoke Suppressant, and Afterglow Suppressant in Polymers," in Fire and Polymers, ACS Symposium Series 425, Chapter 12, American Chemical Society, Washington, 1990.
- 6 Standard Test Method for Surface Flammability of Materials Using a Radiant Heat Energy Source, The American Society for Testing and Materials, ASTM, E 162-83.
- 7 Routley, A.F., "The Development of the Oxygen Index Concept for the Assessment of the Flammability Characteristics of Materials", Central Dockyard Lab., HM Naval Base Portsmouth, Report No. 573, 1973.
- 8 Silvergleit, M., Morris, J.G. and LaRosa, C.N., "Flammability Characteristics of Fiber-Reinforced Organic Matrix Composites", DTNSRDC Report MAT/77/21, June 1977.
- 9 Troitzsch, J, "International Plastics Flammability Handbook", Macmillan Publishing Co., New York, 1983.
- 10 Pitts, J.J., "Inorganic Flame Retardants and Their Mode of Action," in Flame Retardancy of Polymeric Materials, Vol. 1, Chapter 2, Kuryla, W.C. and Papa, A.J., eds., Marcel Dekker, New York, 1973.

- 11 Standard Test Method for Measuring the Minimum Oxygen Concentration to Support Candle-like Combustion of Plastics (Oxygen Index), The American Society for Testing and Materials, ASTM, D 2863-77.
- 12 "Fire Safety Aspects of Polymeric Materials, Volume 2, Test Methods, Specifications and Standards", Technomics Publishing, Westport, CT, 1979.
- 13 Shen, K.K., "Recent Studies on the Use of Zinc Borate as a Flame Retardant and Smoke Suppressant," 8th International Conference on Fire Safety, P. 243, California, 1983.
- 14 Standard Test Method for Specific Optical Density of Smoke Generated by Solid Materials, The American Society for Testing and Materials, ASTM, E 662-83.
- 15 "Fire Protection Handbook", Eds. G.P. McKinnon and K. Tower, Fourteenth edition, Chapter 10, National Fire Protection Association, Boston, Mass, 1976.
- 16 Toxic Gas Sampling and Analytical Procedures Using ASTM E 662 Combustion Modes (basis of Bombardier SMP 800 specification), Boeing BSS 7239, 1983.



Table 1. The Effect of Added Zinc Borate on  $Dm_{(corr)}$  Values and the Measured % Decrease.

RESIN (with 10 phr ZB)	FLAMING MODE		NON-FLAMING MODE	
	$Dm_{(corr)}$	% Decrease	$Dm_{(corr)}$	% Decrease
Derakane 510A	673	12	396	30
Hetron 197AT	414	36	445	22
Hetron 27196	386	37	440	25
Hetron 692TP25	746	-32	330	-3
Epon 813	232	60	203	34

Table 2. Toxic Gas Concentrations by Volume (ppm) as a Function of Added Fire Retardant - Flaming Mode (BSS 7239/ASTM E662).

RESIN	phr ZB	$CO_{1.5min}$	$CO_{4min}$	$CO_{max}$	HCl	HBr
Derakane 510A	0	245	1010	3056	60	62
	10	120	805	2926	72	76
Hetron 197AT	0	320	1160	3328	450	28
	10	180	620	2544	650	10
Hetron 27196	0	160	700	1760	870	7
	10	170	555	2164	4310	3
Hetron 692TP25	0	105	615	2545	150	16
	10	156	630	2866	16	46
Epon 813	0	50	260	870	26	4
	10	32	104	600	8	1

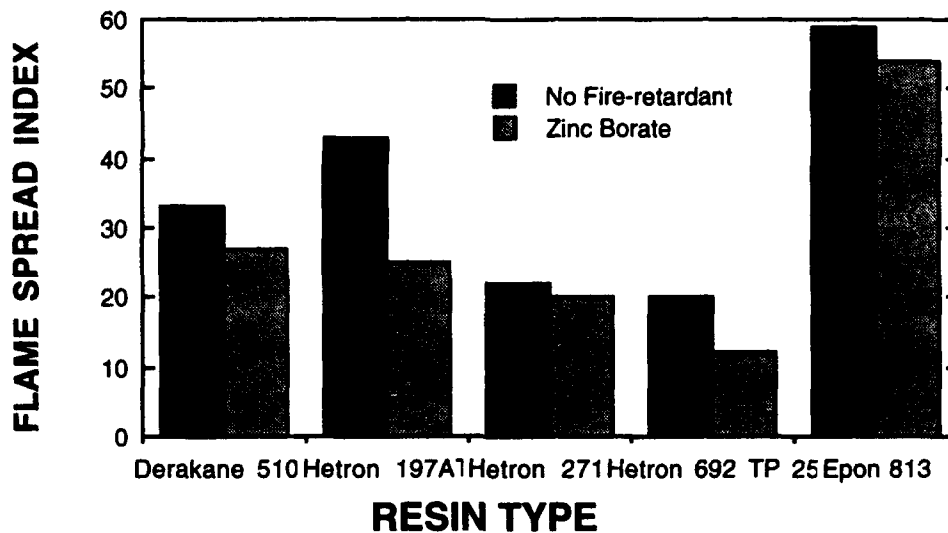


Figure 1. Effect of Added Fire Retardant on the Flame Spread Index (ASTM E 162).

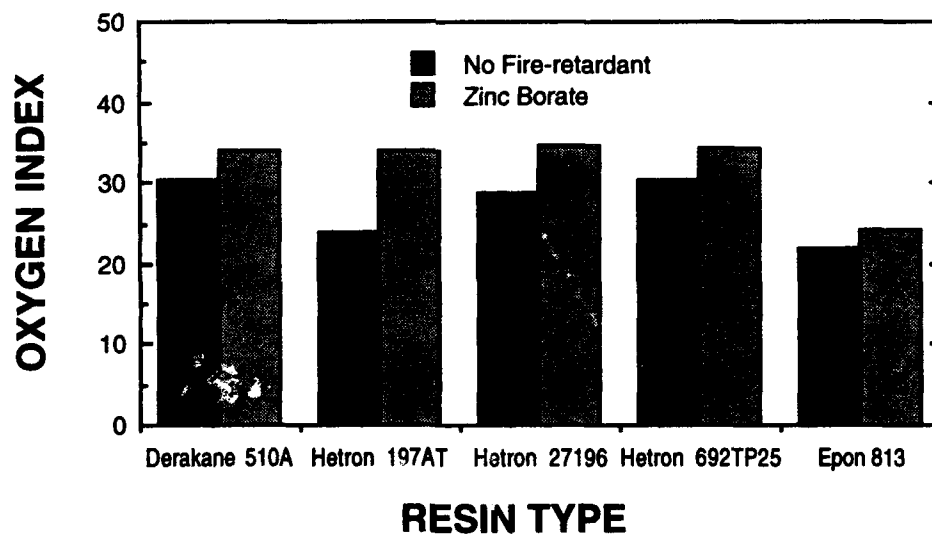


Figure 2. Effect of Added Fire Retardant on the Oxygen Index (ASTM D 2863).

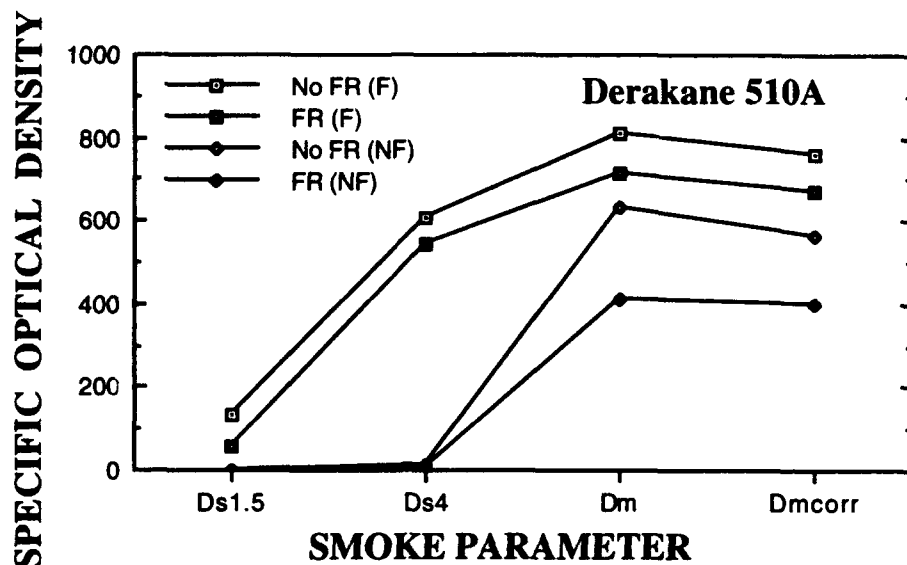


Figure 3. Effect of Added Fire Retardant on the Specific Optical Density (ASTM E 662).

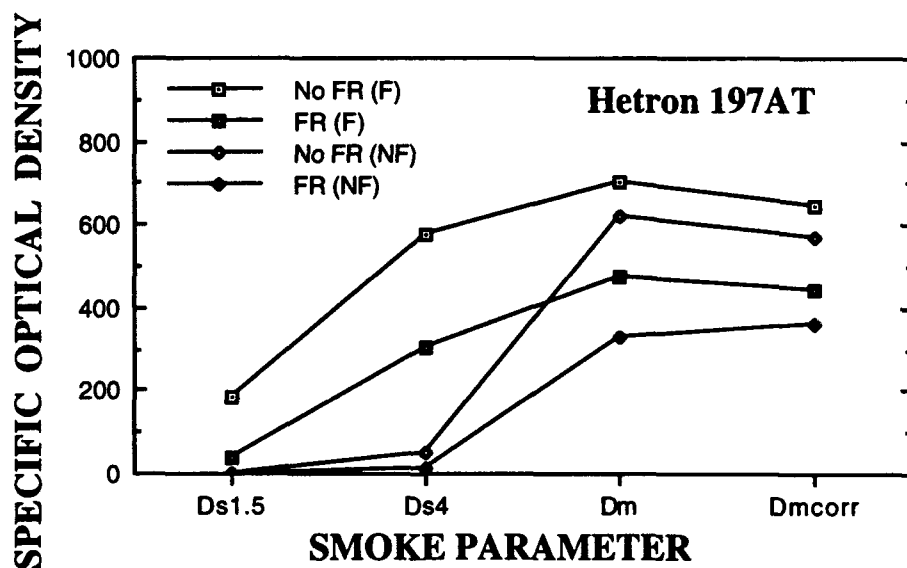


Figure 4. Effect of Added Fire Retardant on the Specific Optical Density (ASTM E 662).

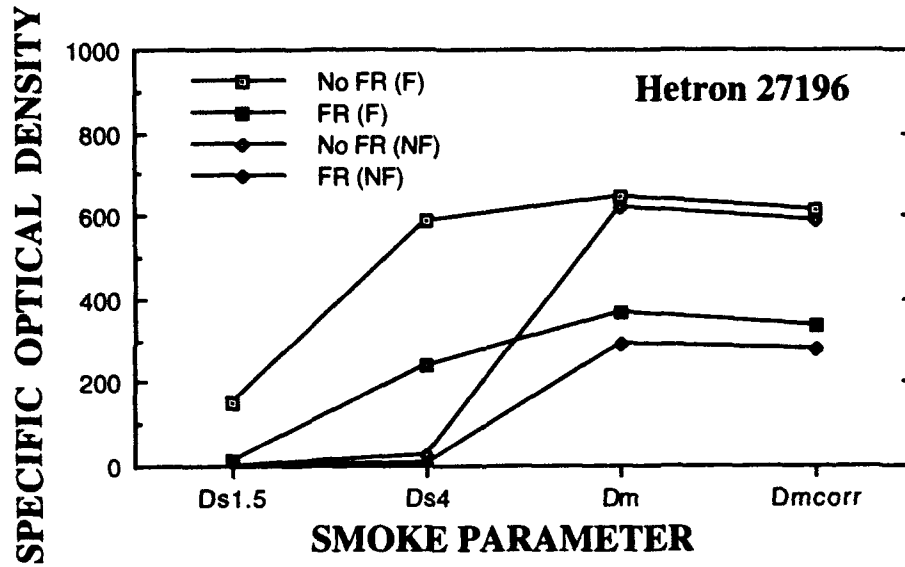


Figure 5. Effect of Added Fire Retardant on the Specific Optical Density (ASTM E 662).

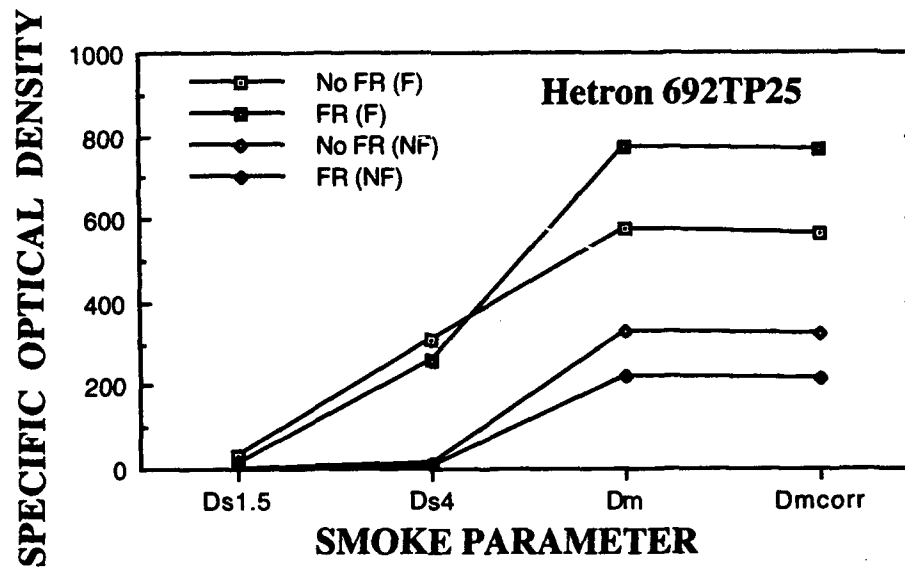


Figure 6. Effect of Added Fire Retardant on the Specific Optical Density (ASTM E 662).

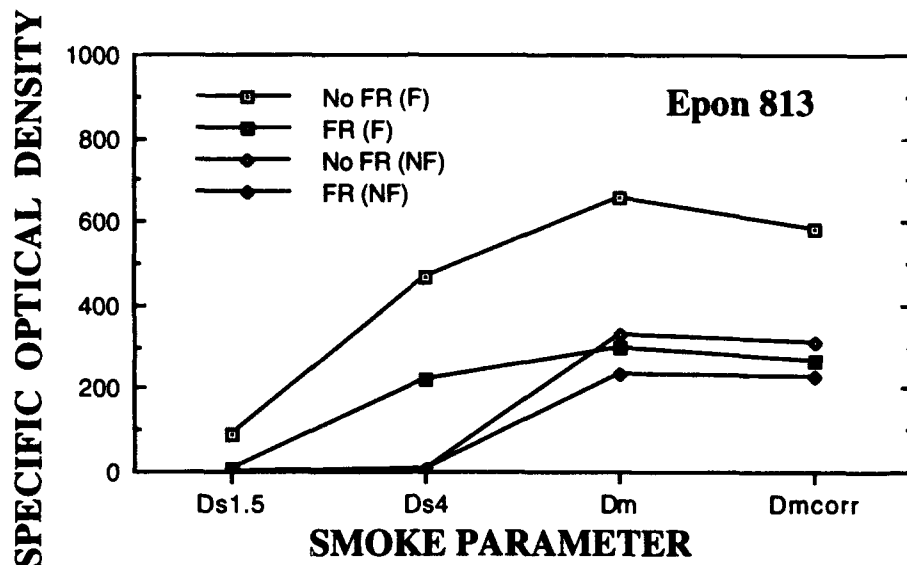


Figure 7. Effect of Added Fire Retardant on the Specific Optical Density (ASTM E 662).

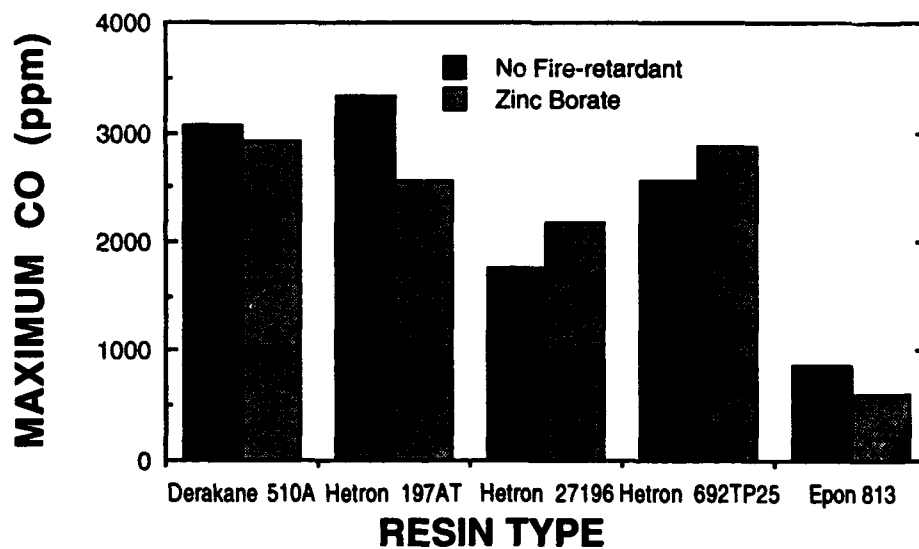


Figure 8. Effect of Added Fire-Retardant on the Concentration of CO<sub>max</sub> (ppm).

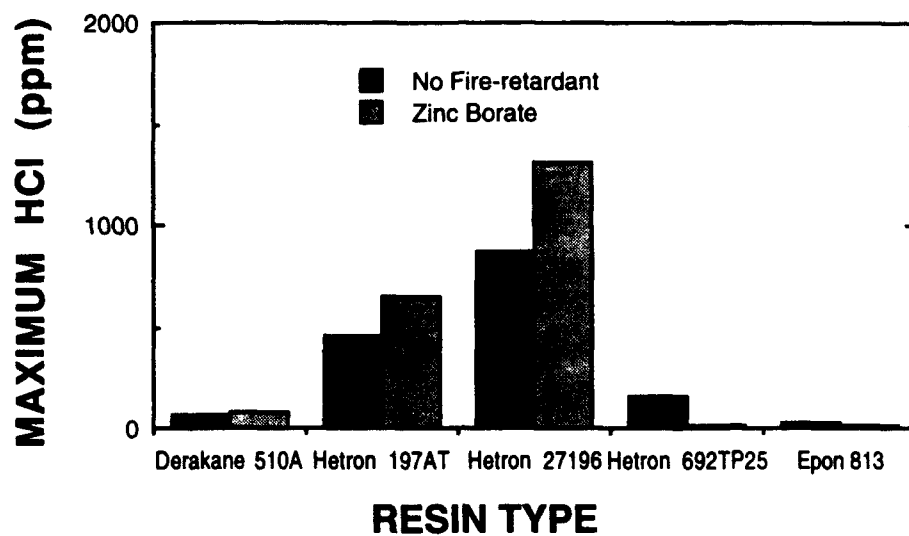


Figure 9. Effect of Added Fire Retardant on the Concentration of  $\text{HCl}_{\text{max}}$  (ppm).

# UNCLASSIFIED

SECURITY CLASSIFICATION OF FORM  
(Highest classification of Title, Abstract, Keywords)

DOCUMENT CONTROL DATA (Security classification of title, body of abstract and indexing annotation must be entered when the overall document is classified)		
<b>1. ORIGINATOR</b> (The name and address of the organization preparing the document. Organizations for whom the document was prepared, e.g. Establishment sponsoring a contractor's report, or tasking agency, are entered in section 8.) <b>Defence Research Establishment Atlantic</b> <b>P.O. Box 1012, Dartmouth, N.S. B2Y 3Z7</b>		<b>2. SECURITY CLASSIFICATION</b> (Overall security of the document including special warning terms if applicable.)  <b>Unclassified</b>
<b>3. TITLE</b> (The complete document title as indicated on the title page. Its classification should be indicated by the appropriate abbreviation (S,C,R or U) in parentheses after the title.)  <b>The Effects of Zinc Borate Addition on the Flammability Characteristics of Polyester, Vinyl Ester and Epoxy Glass Reinforced Plastics</b>		
<b>4. AUTHORS</b> (Last name, first name, middle initial. If military, show rank, e.g. Doe, Maj. John E.)  <b>Morchat, R.M.</b>		
<b>5. DATE OF PUBLICATION</b> (Month and year of publication of document.)  <b>October 1993</b>	<b>6a. NO. OF PAGES</b> (Total containing information. Include Annexes, Appendices, etc.)  <b>23</b>	<b>6b. NO. OF REFS.</b> (Total cited in document.)  <b>16</b>
<b>6. DESCRIPTIVE NOTES</b> (The category of the document, e.g. technical report, technical note or memorandum. If appropriate, enter the type of report, e.g. Interim, progress, summary annual or final. Give the inclusive dates when a specific reporting period is covered.)  <b>Technical Memorandum</b>		
<b>8. SPONSORING ACTIVITY</b> (The name of the department project office or laboratory sponsoring the research and development. Include the address.) <b>Defence Research Establishment Atlantic</b> <b>P.O. Box 1012, Dartmouth, N.S. B2Y 3Z7</b>		
<b>9a. PROJECT OR GRANT NUMBER</b> (If appropriate, the applicable research and development project or grant number under which the document was written. Please specify whether project or grant.)  <b>Project No. 1AI</b>	<b>9b. CONTRACT NUMBER</b> (If appropriate, the applicable number under which the document was written.)  	
<b>10a. ORIGINATOR'S DOCUMENT NUMBER</b> (The official document number by which the document is identified by the originating activity. This number must be unique to this document.)  <b>DREA Technical Memorandum 93/214</b>	<b>10b. OTHER DOCUMENT NUMBERS</b> (Any other numbers which may be assigned this document either by the originator or by the sponsor.)  	
<b>11. DOCUMENT AVAILABILITY</b> (Any limitations on further dissemination of the document, other than those imposed by security classification)  <input checked="" type="checkbox"/> Unlimited distribution <input type="checkbox"/> Distribution limited to defence departments and defence contractors; further distribution only as approved <input type="checkbox"/> Distribution limited to defence departments and Canadian defence contractors; further distribution only as approved <input type="checkbox"/> Distribution limited to government departments and agencies; further distribution only as approved <input type="checkbox"/> Distribution limited to defence departments; further distribution only as approved <input type="checkbox"/> Other (please specify):		
<b>12. DOCUMENT ANNOUNCEMENT</b> (Any limitation to the bibliographic announcement of this document. This will normally correspond to the Document Availability (11). However, where further distribution (beyond the audience specified in 11) is possible, a wider announcement audience may be selected.)  		

# UNCLASSIFIED

SECURITY CLASSIFICATION OF FORM

DDOCS 20047

**UNCLASSIFIED**

SECURITY CLASSIFICATION OF FORM

13. **ABSTRACT** (a brief and factual summary of the document. It may also appear elsewhere in the body of the document itself. It is highly desirable that the abstract of classified documents be unclassified. Each paragraph of the abstract shall begin with an indication of the security classification of the information in the paragraph (unless the document itself is unclassified) represented as (S), (C), (R), or (U). It is not necessary to include here abstracts in both official languages unless the text is bilingual).

The effects of an inorganic fire-retardant additive, zinc borate, on flammability characteristics and smoke generation of glass reinforced polyester, vinyl ester and epoxy resins were evaluated. Information is presented on the flame spread index (ASTM E162), limiting oxygen index (ASTM D2863), density of smoke generated (ASTM E662) and toxic gases of combustion (Boeing BSS 7239).

Results indicated that the addition of 10 phr of zinc borate to the polymeric materials significantly decreased the flame spread index and increased the limiting oxygen index; however, the amount of smoke generated during pyrolytic and flaming combustion was high and unacceptable. Finally, the toxic gas evolution data indicated that the threshold limit values for some gases were exceeded.

14. **KEYWORDS, DESCRIPTORS or IDENTIFIERS** (technically meaningful terms or short phrases that characterize a document and could be helpful in cataloguing the document. They should be selected so that no security classification is required. Identifiers, such as equipment model designation, trade name, military project code name, geographic location may also be included. If possible keywords should be selected from a published thesaurus, e.g. Thesaurus of Engineering and Scientific Terms (TEST) and that thesaurus-identified. If it not possible to select indexing terms which are Unclassified, the classification of each should be indicated as with the title).

ZINC BORATE  
FIRE-RETARDANT  
FLAMMABILITY  
OXYGEN INDEX  
FLAME SPREAD INDEX  
SMOKE GENERATION

**UNCLASSIFIED**

SECURITY CLASSIFICATION OF FORM